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Preparation and Structural Characterization of Transition-Metal Complexes Featuring the Cymantrenyl(bromo)boryl Ligand

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In the present paper, we describe the first structural characterization of cymantrenyl(dihalo)borane and report on its use for the synthesis of novel cymantrenylboryl complexes.

The chemistry of transition-metal boryl complexes [L_xM-BR_2], and in particular the nature of the metal−boron linkage, has been the subject of intense research for well over a decade.[1] Most recently, we have started to investigate the potential of ferrocenyl(dibromo)borane ($FcBBr_2$) for the synthesis of complexes of the type [$L_xM-B(Br)Fc$][2] and [$L_xM-B(Fc)M'L_x$].[3] Our interest in this long-known borane and its derivatives[4] is based on more recent studies, which established a correlation between the electronic stabilization of the boron atom provided by the iron center and the geometry of the molecule, i.e., bending of the *exo*-BR_2 group toward iron. The latter deviation from planarity is usually expressed by the dip angle α^* ($\alpha^* = 180° - \alpha$, with α being the angle between the centroid of the substituted Cp ring, the ipso carbon, and the boron atom).[5] Because α^* is dependent on the Lewis acidity of the boron center, and, hence, on the degree of π backbonding possibly provided by the boron-bound substitutents, we found the Fc moiety to be a useful tool for probing transition-metal boron $d_\pi-p_\pi$ interactions in boryl complexes.[2,3] Current studies address the question of whether corresponding half-sandwich complexes, derived from cymantrene [$(\eta^5\text{-}C_5H_5)Mn(CO)_3$] or methylcymantrene [$(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$], exhibit a similar stabilizing effect on Cp-bound BR_2 groups and, consequently, can be utilized for the synthesis of cymantrenylboryl complexes. In the present paper, we report the first structural characterization of a cymantrenyl(dibromo)borane derivative and corresponding boryl complexes obtained from its reactions with $M[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ ($M = K$, $R = H$; $M = Na$, $R = Me$).

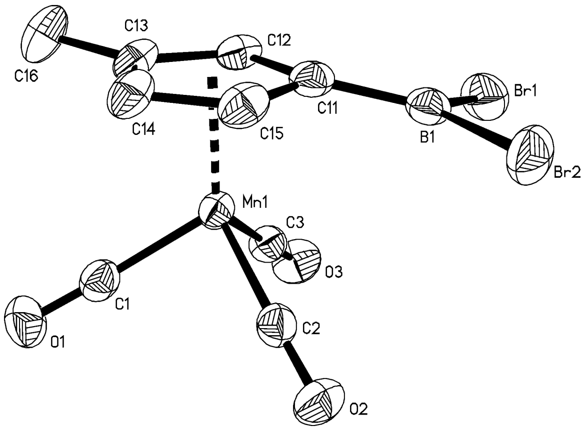

Figure 1. Molecular structure of **2**. Relevant bond lengths (Å): $B1-Br1 = 1.920(4)$, $B1-Br2 = 1.915(4)$, $C11-B1 = 1.504(4)$.

Cymantrenyl(dibromo)borane (**1**) and methylcymantrenyl-(3-dibromo)borane (**2**) were obtained similarly to procedures already described 30 years ago by Siebert and co-workers and isolated as low-melting products of oily appearance.[6]

In the case of **1**, all attempts to obtain single crystals suitable for X-ray analysis notoriously failed. From concentrated hexane/toluene solutions of the methylcymantrenyl derivative **2**, however, dark-orange, very air- and moisture-sensitive crystals could be grown within 6 weeks at −30 °C. Compound **2** crystallizes in the space group *Pbca*, and the molecule adopts C_1 symmetry (Figure 1). The structural data prove that borylation occurred at the β position of the cyclopentadienyl ring, as was already predicted by Siebert on the basis of spectroscopic data.[4] The most important structural feature

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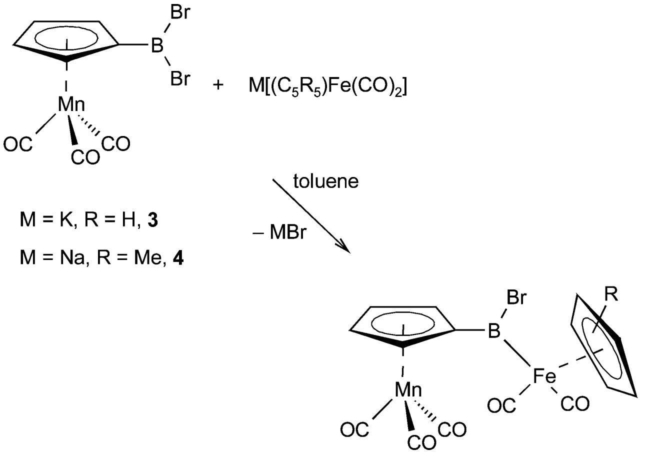
Scheme 1



in **2** is the bending of the *exo*-boryl group toward the manganese center. With a dip angle of 12.3°, the deviation from planarity is less pronounced than that in $FcBBr_2$ (17.7° and 18.9°) but still significant.[5b] The reduced value of α^* for **2** in comparison to $FcBBr_2$ is supposed to be due to the presence of the three electron-withdrawing CO ligands in the former.

Further differences in the structural parameters, e.g., with respect to the B−M distances, can be attributed to the different covalent radii of the transition metal (manganese vs iron).

The boryl complexes $[(\eta^5\text{-}C_5H_5)(OC)_2Fe\{B(Cym)Br\}]$ (**3**) and $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{B(Cym)Br\}]$ (**4**) (Cym = cymantrenyl) were obtained in yields of 46% (**3**) and 34% (**4**) by salt elimination reactions between **1** and $K[(\eta^5\text{-}C_5H_5)(OC)_2Fe]$ (KFp) and $Na[(\eta^5\text{-}C_5Me_5)(OC)_2Fe]$ (NaFp*), respectively (Scheme 1).

For both complexes, the characteristic multinuclear NMR spectroscopic data were observed. **3** displays three signals in the ^1H NMR spectrum, a singlet at 4.18 ppm for the protons of the Fp fragment and two multiplets at 4.23 and 5.13 ppm for the protons of the cymantrenyl group. These signals correlate to the signals found in the ^{13}C NMR spectrum at 85.9 (Fp), 86.4, and 95.0 (Cym) ppm. Furthermore, the carbon signals for the carbonyl groups were observed at 214.6 (Fp) and 224.8 (Cym) ppm. In the ^{11}B NMR spectrum, a signal at 102.2 ppm can be found, which is shifted downfield with respect to that of **1**. The Cp* derivative **4** is characterized by similar spectroscopic data and displays, e.g., in the ^1H NMR spectrum, a resonance at 1.42 ppm (9.9 ppm) for the Cp* moiety and two multiplets at 4.22 and 5.21 ppm (86.2 and 94.1 ppm) for the boryl-substituted Cp ring (protons corresponding to carbon signals are given in parentheses). In addition, two signals in the ^{13}C NMR spectrum for the carbonyl groups at 216.4 (Fp*) and 224.8 (Cym) ppm are observed, and the ^{11}B NMR spectrum shows a deshielded signal at 106.1 ppm.

In the IR spectra, recorded as a toluene solution, compounds **3** and **4** exhibit carbonyl stretching bands at relatively high wavenumbers (2045, 2024, 1999, and 1940 cm^{-1} for **3**; 2023, 1976, and 1923 cm^{-1} for **4**), which fall in the same range as those reported for the ferrocenyl-substituted boryl complexes $[(\eta^5\text{-}C_5R_5)(OC)_2Fe\text{-}B(Br)Fc]$ (R = H, Me).[2a] A direct assignment of the five expected bands (three for the Cym fragment and two for the Fp or Fp* fragment) is hampered by the broad and, hence, overlapping appearance of the bands.

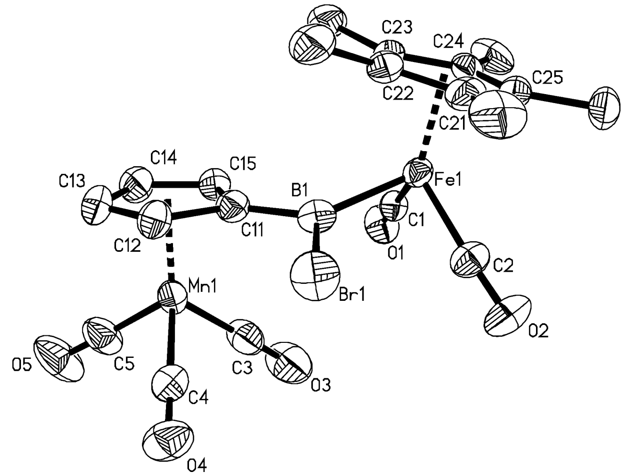


Figure 2. Molecular structure of **4**. Relevant bond lengths (Å): Fe1−B1 = 1.983(4), Br1−B1 = 1.981(4), C11−B1 = 1.539(6).

By recrystallization of **4** from a concentrated toluene solution, suitable crystals for a crystallographic analysis were obtained. **4** crystallizes in the space group *Pbca* and the molecule adopts C_1 symmetry (Figure 2).

The structural parameters for **4** are similar to those of the ferrocenyl derivative $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{B(Fc)Br\}]$ (**5**).[2a] In particular, the two planes, defined by $B1-Fe1-Cp_{Fp}^{centroid}$ and B1−C11−Br1, respectively, are oriented almost perpendicular to each other (88.7°), as was already observed for **5**. Likewise, the distances between boron and iron are almost identical with 1.983(4) Å for **4** and 1.972(3) Å for **5**, respectively, as is the distance between boron and the ipso carbon [1.539(6) Å]. The dip angle α^* found for **4** amounts to only 1.1°, thus indicating virtually no bending of the iron-substituted boryl group toward the manganese center. Hence, α^* in **4** is approximately 11° smaller than that in the dibromoborane **2**. The same difference of 11° was found between $FcBBr_2$ and **5**. Both the decreased dip angle α^* and the similarly short B−Fe bond lengths indicate a $d_\pi-p_\pi$ stabilization from the iron to the Lewis acidic boron center. Accordingly, short B−Fe bond lengths due to π interaction have been found in aryl(halo)boryl complexes, namely, $[(\eta^5\text{-}C_5R_4R')(OC)_2Fe\{B(2,4,6\text{-}Me_3C_6H_2)Br\}]$[7] [R = R′ = H, **6a**, 1.964(5) Å; R = H, R′ = Me, **6b**, 1.962(4) Å; R = R′ = Me, **6c**, 1.972(2) Å] and $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{B(Ph)Cl\}]$[8] [**7**, 2.005(10) Å]. In contrast, significantly greater B−Fe separations were documented for amino-substituted boryl complexes, such as $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{B(Me_2N)Cl\}]$[9] [**8**, 2.027(5) Å], $[(\eta^5\text{-}C_5H_5)(OC)_2Fe\{B(Me_2N)B(NMe_2)Cl\}]$[10] [**9**,

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2.090(3) Å], and [{(η^5-C_5H_4Me)$(OC)_2Fe$}$_2$($B_3N_3H_3Cl$)][11] [**10**, 2.045(1) Å]. The longer B−Fe bond lengths in the latter compounds are attributed to the electron-donating amino substituents, which mediate the Lewis acidity of the boron atom and, hence, impose a reduced Fe−B interaction.

In conclusion, the first structural characterization of a cymantrenyl(dihalo)borane indicates an, albeit less significant, metal−boron interaction, as was already observed for related ferrocenyl(dihalo)boranes. $CymBBr_2$ was successfully employed for the synthesis of the first cymantrenyl-substituted boryl complexes, and structural data reveal the similarity between the ferrocenyl and cymantrenyl substituents. Further cymantrenyl-substituted boryl complexes are subject to ongoing studies in our laboratory.

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Supporting Information Available: X-ray crystallographic data in CIF format, experimental procedures, crystal data and structural refinement, hydrogen and atomic coordinates, displacement parameters, and bond lengths and angles for compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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